

JAPANESE PATENT OFFICE (JP)

PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. SHO 62[1987]-83471

Int. Cl. ⁴ :	C 23 C 16/26 C 08 J 7/00 C 23 C 7/06 16/50
Identification code:	306
Sequence Nos. for Office Use:	6554-4K 7206-4F 7206-4F 6554-4K
Application No.:	Sho 60-223547
Application Date:	October 9, 1985
Publication Date:	April 16, 1987
No. of Inventions:	2 (Total of 5 pages)
Examination Request:	Not requested

FORMATION OF CARBON FILM AND THE DEVICE USED

[Tan'sohimakukeiseihoho oyobi souchi]

Applicant:	Hitachi Corp. 4-6 Surugadai, Kanda Chiyoda-ku, Tokyo
------------	--

Inventors:

Yuichi Otsuno
Ryo Kito
Yoshinori Honda
c/o Hitachi Corp.
Prod. Tech. Center
292 banchi, Yoshida-machi
Tozuka-ku, Yokohama-shi

Agent:

Masao Ogawa
Patent attorney
and 1 other

[There are no amendments to this patent.]

Specification

1. Title of the invention

Formation of a carbon film and device used

2. Claims of the invention

1. Formation of a carbon film wherein a film base is wrapped around a grounded rotary electrode, and a high-frequency voltage is applied to the counter electrode opposite to the treatment position of the rotary electrode to maintain a plasma, the area of the above mentioned counter electrode is made sufficiently larger than the area of the part to be treated on the rotary electrode so that the average value of the surface potential for the part is a large negative value compare to the average value of the plasma potential; thus, high-energy ions impinge on the surface of the part and form a film.

2. The method of manufacturing a carbon film specified in claim 1 above wherein either a hydrocarbon gas or a gas mixture consisting of a hydrocarbon gas and hydrogen gas is used as the reactive gas, and the film produced is a hard carbon film made of a hydrogen-containing amorphous or fine crystal-containing amorphous structure.

3. A device used for formation of a carbon film equipped with a supply roll used for continuous supply of a film-like base material, and a wind-up roll, a grounded rotary electrode around which a film base is wrapped, and a counter electrode having an adequately larger area than the area treated formed at the opposite to the rotary electrode.

3. Detailed explanation of the invention

[Field of industrial application]

The present invention pertains to a formation of a hard carbon film continuous on the surface of a film base material at a high speed and a device used.

[Background of the invention]

It is known that a hard film commonly referred to as a diamond-like carbon film or i-carbon is produced under a certain conditions when decomposition is carried out for a hydrocarbon gas such as methane using a glow discharge energy. The hard carbon film produced has high electrical insulation properties, high infrared permeability, high refractive index, high abrasion resistance, and low coefficient of friction, etc., and can be applied to a varieties of

purposes. From the standpoint of high abrasion resistance, applications to magnetic heads, magnetic disks, optical lenses, carbide tools, etc. can be mentioned.

[p. 2]

When it is possible to deposit the above mentioned hard carbon film onto the surface of a film base material efficiently, it can be used as abrasion resistance protective layer for magnetic tapes and floppy disks.

When a conventional method of manufacturing a hard carbon film is used, it is not possible to use for the film base material application. In other words, to produce a hard carbon film, the film formation is carried out as a high energy ion is applied to the surface of the base material or the film formation is carried out as the base material is heated to a temperature of at least 600°C. In the case of the former, a method where deposition of carbon is carried out as a hydrogen ion is applied to the base material is disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-55319, and a method where direct current bias voltage is applied to the base material and an accelerated ion is applied to the surface of the base material is disclosed in Japanese Kokai Patent Application No. Sho 59[1984]-35092. However, in the case when a film is produced onto a insulation film-like base material, application of a bias voltage to said base material is not possible, and when ion is applied, abnormal discharge occurs due to accumulation of the charge or instable film material is produced, and many other problems surface. On the other hand, when the latter method where the base material is heated, in many cases, the film is made of an organic polymer material and the heat resistance is inadequate, thus it is not possible.

As a method of formation of a carbon film without accumulating charge in the insulation base material, use of high-frequency plasma can be mentioned. As described in the references (L. Holland and S.M. Ojha, Thin-Solid [phonetic] Films, vol. 38, L17 (1976)), when decomposition is carried out for hydrocarbon gas with a high-frequency bipolar discharge, a hard carbon film can be produced. In a high-frequency plasma, the positive and negative charge migrate into the base material during one cycle of the voltage oscillation is neutralized, thus, danger of an increase in the charge is absent.

However, application of the above mentioned high-frequency plasma method to a film-like base material, many problems exist. In order to perform continuous treatment of a film-like base material, the film is wrapped around the surface of a rotary cylindrical drum, and a treatment is carried out in one area of the above mentioned rotary drum and winding of the base material is synchronized with the rotation of the rotary drum, but when a high-frequency voltage is applied to the rotary drum,

- 1) The mechanism becomes complex because high voltage must be applied to a rotating body.
- 2) Unwanted discharge may occur because areas other than the treatment area of the rotary drum are charged to a high voltage.
- 3) When a thin metal film is formed on a film base such as in the case of a magnetic tape, it is necessary to apply a high voltage to the thin metal film itself, but the potential of the supply and receiving mechanism also increase, and the insulation

system becomes complicated.

etc.

[Objective of the invention]

The objective of the present invention is to provide a method for stable and continuous formation of a hard carbon film on the surface of a film-like base material using a high-frequency plasma without any of the above mentioned problems that exist with current technology, and to provide a device for achieving said objective.

[Outline of the invention]

The present invention is a method of formation of a carbon film wherein a rotary electrode around which a film base is wrapped is grounded, high-frequency voltage is applied to a counter electrode opposite the position on the rotary electrode that is being treated to maintain a plasma, the area of the above mentioned counter electrode is made sufficiently large compared to the area of the part being treated on the rotary electrode so that the average value of the surface potential of the part being treated is a large negative value compared to the average plasma potential; thus, high-energy ions impinge on the surface of the part to form a film.

As a device used to apply the method described above, a supply roll for continuously supplying the base material film and a receiving roll are installed, and a grounded, rotary electrode is used for formation of the film as the film base material supplied and wound on a

take-up roll. A counter electrode is position opposite the above mentioned rotary electrode. The above mentioned counter electrode is an electrode having a sufficiently large surface compared to the surface where the plasma is applied to the rotary electrode.

[Application examples of the present invention]

In the following, an application example of the present invention is explained in detail.

First, the device used is explained with Figure 1.

[p. 3]

In the figure, the device has a structure consisting of vacuum chamber 1 and vacuum exhaust mechanism 2, a film supply mechanism, plasma treatment chamber 3, high-quality voltage application mechanism 4, and reaction gas supply mechanism 5. The film supply mechanism has a structure consisting of film supply roll 7 that supplies film 6, rotary electrode 8, wind-up roll 9, and guide rolls 10 that provide stable film tension and prevent formation of wrinkles, and a power system that operates the above mentioned mechanism, and a rotational speed adjustment mechanism. Counter electrode 11 and reactive gas induction inlet 12 and exhaust port 13 are built into plasma treatment chamber 3. In order to provide a uniform supply of the reactive gas to treatment chamber 3, for example, many small holes 14 are formed on counter electrode 11 as shown in Figure 2, and gas is blown from these holes. In order to prevent the temperature of rotary electrode 8 and counter electrode 11 from increasing as a result of the heat generated by the plasma, a water cooling system is used.

Rotary electrode 8 is ground with vacuum chamber 1.

Also, the area of electrode 11 is made sufficiently larger than the area where plasma is applied to rotary electrode 8.

In the following, the film formation method using the above mentioned device is explained.

In the application example, rotary electrode 8 is used as the grounded electrode, and a high-frequency voltage of 100 KHz to 100 MHz is applied to counter electrode 11 to maintain a plasma of hydrocarbon or a gas mixture comprised of hydrocarbon and hydrogen, and a carbon film is produced on the surface of the film-like base material opposite the electrode on the grounded side (rotary electrode 8). The main feature of the present invention is that the area of counter electrode 11 is larger than the area of the rotary electrode 8 to be treated (ground side electrode). In high-frequency discharge in the above mentioned frequency range, the speed of the electrons is much higher than the speed of positive ions, as a result, the sheath voltage drop changes according to the ratio of effective areas of the two electrodes, and the voltage drop of the electrode with the smallest area increases. However, the above mentioned effective area means the area that is in contact with the plasma. Thus, when the area that is in contact with the plasma is increased in comparison to the treated area of rotary electrode 8 (ground side electrode), the plasma potential becomes higher than the potential of the treated surface, and a condition where high-energy ions impinge on and are embedded in the treated surface is created, and a hard carbon film can be produced.

The effective area ratio of the above mentioned rotary electrode 8 (ground side electrode), and counter electrode 11 is at least 1:3, and at least 1:5 is preferable. Furthermore, a high-frequency voltage with an amplitude of at least 1 KV is desirable.

For the above mentioned hydrocarbon, gases or vapors of the substances shown below can be used.

- 1) Saturated aliphatic hydrocarbons such as methane, ethane, propane, and butane
- 2) Unsaturated aliphatic hydrocarbons such as ethylene, acetylene, propene, butene, and butadiene
- 3) Aromatic hydrocarbons such as benzene, naphthalene, toluene, ethyl benzene, etc.

The hard carbon film produced in the present invention is a hydrogen-containing amorphous carbon film or fine crystal-containing carbon film with an amorphous structure, and a hard film having a Vicker's hardness of at least 1000, which is less likely to wear out, can be produced.

In the following, formation of the hard carbon film by the method of the present invention is explained in specific terms when the film is applied as a protective film in the formation of a deposition-type magnetic tape.

A base material produced by depositing a Co/Ni-alloy thin magnetic film having a thickness of 0.1 μm on one surface of a polyester film having a thickness of 10 μm was arranged in the device shown in Figure 1. Then, a pre-exhaust treatment was carried out for vacuum chamber 1 and treatment chamber 3 to produce a vacuum of 1×10^{-3} Pa or less, benzene vapor

was supplied at a constant flow rate, and the exhaust speed was adjusted, and the pressure in treatment chamber 3 was kept at 0.05 Torr. The film was then supplied at a rate of 5 m/min, and a high-frequency voltage of 13.56 MHz with an amplitude of 2 KV was applied to counter electrode 11, and a plasma was formed. As the result of a continuous three-hour treatment, a hard carbon film with a thickness of 200 Å was uniformly produced over the entire surface of the film for a length of 900 m. No abnormal discharge was observed during the above treatment. The magnetic tape treated as described above was slit to a width of 8 mm, and set-up for a VTR recorder, sticking of the tape and unstable operation were not observed, and a significant increase in life of the tape was observed.

[p. 4]

Figure 3 shows a different application example, and wherein a device with multiple treatment chambers arranged around a rotary drum is used and the treatment speed is increased. In this type of device, a multilayer film can be produced by changing the treatment conditions or type of reactive gas used, and the structure of specific treatment chambers can be changed, and different types of treatments such as plasma cleaning, etching, sputtering, and deposition can be carried out at the same time, as described for formation of the hard carbon film mentioned above. When high voltage is applied to rotary electrode 8, the above-mentioned multifunctions cannot be achieved. Thus, the above mentioned multifunction performance is based on grounding of rotary electrode 8.

[Effect of the invention]

As described in detail above, according to the present invention, the rotary electrode is grounded, and a high-frequency voltage is applied to the counter electrode and a plasma is formed and contained; thus, formation of unwanted discharge or problems with insulation can be avoided.

Furthermore, the area that is in contact with the plasma is increased in comparison to the treated area of the rotary electrode (ground side electrode), the plasma potential is higher than the treated surface, and a condition wherein high energy ions impinge on and are imbedded in the treated surface is created, and a hard carbon film can be easily produced.

4. Brief description of figures

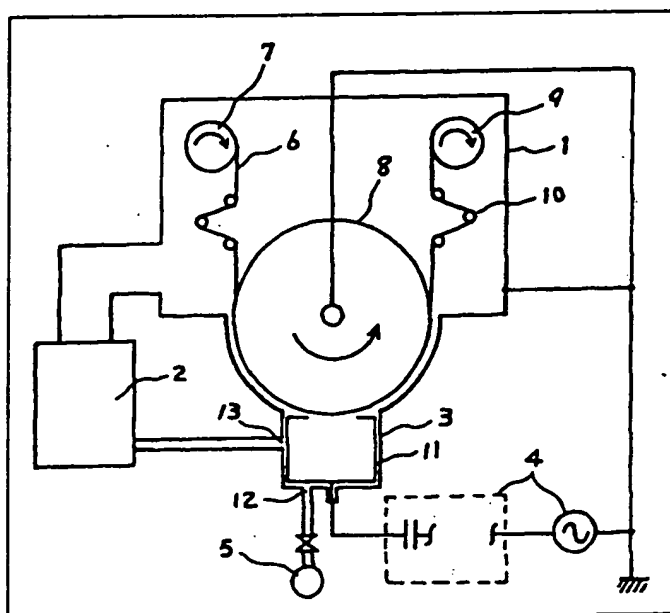
Figure 1 is an application example of the present invention, and shows the over-all structure of the device used for formation of the hard carbon film of the present invention.

Figure 2 is a partial structural view of the counter electrode. Figure 3 is a view that shows the over-all structure of a different application example of the present invention.

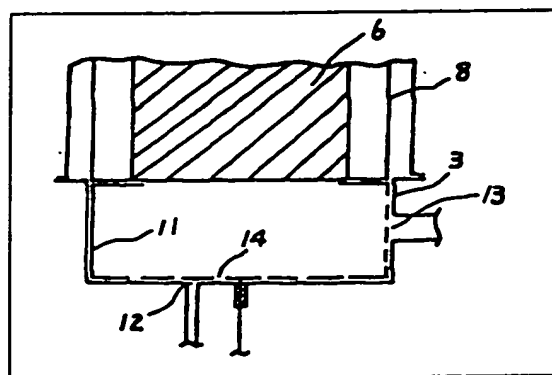
Agent: Masao Ogawa, patent attorney

- 7 ... Supply roller
- 8 ... Rotary electrode
- 9 ... Receiving roll
- 11 ... Counter electrode

[Figure 1]



[Figure 2]



[Figure 3]

